Kentucky Method 64-224-03
Revised 1/6/03
Supersedes KM 64-224-00
Dated 10/09/00

CHEMICAL ANALYSIS OF LIMESTONE, FINE AGGREGATE, QUICKLIME AND HYDRATED LIME

1. SCOPE: This test method covers aggregate intended for use in various highway construction projects. Chemical analysis of aggregates are required only when specified on plans, proposals, bidding invitations, or by special provisions covering any particular material or projects. This method is a modification of ASTM C-25 for the chemical testing of limestone, fine aggregate, quicklime and hydrated lime by x-ray spectroscopy.

2. APPARATUS AND MATERIALS:

   2.1. Wet Chemical: All wet chemical analysis will be performed in accordance with ASTM C-25 current edition ~~-95b~~.

   2.2. X-Ray Fluorescence:

      2.2.1. Philips MagiX PRO Wavelength ~~Kevex Analyst 771 Energy~~ Dispersive X-Ray Fluorescence Spectrometer

      2.2.2. SuperQ ~~WinXRF 2.40~~ software

      2.2.3. Philips Perl'x 3 fused bead machine ~~Spex 31 mm Die Set.~~

      2.2.4. Platinum dish and crucible set ~~Hydraulic Press with a 25 Metric-Ton Maximum~~.

      2.2.5. Spex 8000 Mixer/Mill

      2.2.6. Lithium Bromide (LiBr) – 10% solution non-wetting agent

      2.2.7. 100% Lithium Tetraborate ($Li_2B_4O_7$) flux

3. SAMPLE: A maximum 0.95 liter (quart) sample is provided by the section requesting the analysis.

4. PROCEDURE:

   4.1. Prepare porcelain crucibles by igniting at 950°C to constant weight. Cool and store crucibles in dessicator to avoid absorption of moisture.

   4.2. Weigh 1.0 gram of sample accurately to 0.0001 grams into a prepared porcelain crucible. Ignite sample to a constant weight in a muffle furnace at 950°C and cool in a dessicator.

   4.3. Calculate the loss on ignition(LOI) using the following formula:

LOI = (A/B) x 100
where:
A = weight of sample after ignition;
B = weight of original sample

4.4. Place at least 1.0 gram of the original sample in the spex 8000 mixer/mill and grind until fine powder is obtained and/or sample is completely uniform. This takes approximately 30 seconds.

4.5. Weigh accurately to 0.0001 grams 6.0 grams of flux directly into platinum crucible. Then weigh accurately to 0.0001 grams 0.6 grams of original sample from spex 8000 mixer/mill directly into the platinum crucible. Add 3 drops of LiBr solution. Place the platinum crucible and dish in the Perl'x3 machine and select to run program 9* for all types of limestone, aggregate and lime. This takes approximately 15 minutes. Program run is dependent on sample type.

4.6. Enter names of samples and LOI information in measure sample screen on the measure and analyze program.

4.7. Place sample in a 27mm steel cup. Then place in x-ray instrument and prepare to run lime or ledgerock application on the measure sample screen. Click on measure at the bottom of the screen. This may take a few minutes. The application chosen is dependent upon the sample type.

~~4.1 Preparation~~

~~4.1.1 The sample as received may be either wet or dry. If it is wet, it should be dried by placing it on absorbent paper and letting it stand overnight at room temperature, or by heating it in a pan on a hot plate with occasional stirring until no moisture is evident.~~

~~4.1.2 The sample should be quartered until it is reduced to 10 - 20 grams. Grind this until the entire sample passes a 300 µm (No. 50) sieve. Transfer to a sample jar, mix well, and cover with screw cap.~~

~~4.1.3 If the sample is received in seed envelope. already in powder form, the 0.5 gram sample may be weighed without further preparation.~~

~~4.2 Chemical Analysis~~

~~4.2.1 Insolubles~~

~~4.2.1.1 Weigh to analytical accuracy, or four decimal places, a 0.5 gram sample, and transfer to a porcelain casserole. Carefully add 20 ml of HC1 (1:1) by pouring down the inside surface of the casserole. Place on asbestos pad, or hot plate, and carefully evaporate to dryness. Remove from hot plate, and~~

cool to room temperature. Add 20 ml of HC1 (1:1). Place casserole on hot plate, and add 50 - 75 ml of distilled water. Stir gently while heating until all soluble material is in solution. Continue heating until sample comes to boil. Filter through 425 µm (No. 40) filter paper into a 400 ml beaker. Wash with hot water, and save total filtrate. Transfer filter paper containing residue into a platinum crucible, which was previously weighed accurately. Char, ignite, and ash residue in muffle furnace for one hour. Cool in desiccator, and reweigh.

4.2.1.2 Calculations

Weight Ash x 100 ÷ Sample Weight = % Insolubles.

Where "100" is used to convert weight fraction insolubles in sample to percent insolubles in sample.

4.2.2 Silica

4.2.2.1 To the ash reserved from insoluble determination, add a drop or two of distilled water to moisten. Add one drop of concentrated H2SO4. Carefully add about 15 ml of concentrated HF. CAUTION Avoid spilling, or splashing of, or bodily contact with, this highly corrosive reagent. Burn injury to body tissue will inevitably be deep and severe. Place crucible on asbestos pad on hot plate in exhaust hood, and evaporate to dryness. Remove from hot plate, and cool to room temperature. Add another 15 ml portion of HF, and again evaporate to dryness. When crucible and residue contained are thoroughly dry, burn in bright red muffle furnace for 15-30 minutes. Cool in desiccator, and reweigh.

4.2.2.2 Calculations

$$\frac{Loss\,of\,Weight\ x\ 100}{Sample\,Weight} = \%\ SiO_2$$

Where "100" is used to convert weight fraction SIO_2 in sample to percent SiO_2 in sample.

4.2.3 R_2O_3 (Ammonium Hydroxide Group)

4.2.3.1 To filtrate reserved from (4.2.1), add 3 drops of methyl red indicator. Add 20 ml of NH_4C1 (20g/L) solution, and make basic with NH_4OH. Heat to boiling on hot plate, and allow to boil for 2-3 minutes. Filter while hot on No. 541 filter paper into a one-liter flask, and wash residue with hot distilled water. Reserve filtrate for next determinations. Place filter paper and precipitate in pre-weighed porcelain crucible, char on hot plate and burn in red muffle furnace for 1 hour. Cool in desiccator, and weigh. Gain in weight is R_2O_3.

4.2.3.2 Calculations

Where "100" is used to convert weight fraction R_2O_3 in sample to percent R_2O_3 in sample.

4.2.4 Calcium Carbonate

4.2.4.1 Reserve filtrate from R_2O_3 determination in a 400 ml beaker. Acidify with HC1, heat to boiling on hot plate, add 40 ml of hot, saturated ammonium oxalate solution. Remove from hot plate and immediately return to alkaline indication by adding ammonium hydroxide. Allow precipitate to settle for 4 hours at a temperature below boiling, and filter through No. 42 paper into a 400 ml beaker. Wash precipitate with cold distilled water, and save total filtrate. Transfer filter paper containing residue to porcelain crucible, which was previously weighed accurately. Char, ignite, and ash residue in muffle furnace for 1 hour. Cool in desiccator, and re-weigh.

4.2.4.2 Calculation

* Where "100" is used to convert weight fraction $CaCO_3$ in sample to percent $CaCO_3$ in sample.

** Analysis expressed as % CaO: insert "1.000" in place of "1.785" where "1.785" is molecular weight ratio value for (mol. wt. $CaCO_3$): (mol. wt. CaO).

4.2.5 Magnesium Carbonate

4.2.5.1 To filtrate reserved from calcium carbonate filtration, add HC1 until acid. Then add 20 ml disbasic ammonium phosphate solution (20 grams per liter). Make alkaline with ammonium hydroxide, and stir vigorously until precipitate is formed. Allow precipitate to settle overnight. Filter through No. 42 filter paper into a 400 ml beaker. Wash precipitate with cold distilled water. Transfer filter paper containing residue to porcelain crucible, which was previously weighed accurately. Char, ignite, and ash residue in muffle furnace for 1 hour. Cool in desiccator, and re-weigh.

4.2.5.2 Calculation

* Analysis expressed as MgO: insert "0.3620" in place of "0.7575".

Where "0.7575" is molecular weight ratio value for (mol. wt. $MgCO_3$): (mol. wt. MgP_2O_7).

Where "100" is used to convert weight fraction $MgCO_3$ in sample to percent $CaCO_3$ in sample.

4.3 Alternate X-Ray Fluorescence

4.3.1 Grind the dry sample until it passes a 300 µm (No. 50) mesh sieve.

4.3.2 Weigh to 0.0001 gm, a 6.5 gram sample. Weigh to 0.0001 gm, a 0.6 gram aliquot of polyvinyl alcohol. Grind the two aliquots together in a Spex Mixer/Mill. Press into a pellet in a 31 mm die set on the hydraulic press at 16.5 metric tons.

4.3.2.1 Calculation

Weight Polyvinyl Alcohol/ Weight Sample = Added Sample Ratio

4.3.3 Acquire spectra under the conditions listed in Table 1. Process escape peaks. Subtract the background automatically modeled by the software. Perform the gaussian deconvolutions specified in Table 2 for each condition. Save the intensities.

4.3.4 Rotate the sample one third turn, and repeat step 4.3.3

4.3.5 Rotate the sample another one third turn, and repeat 4.3.3.

4.3.6 Quantify by the exact program against a standard with a similar matrix. Average the three sets of data in order to compensate for possible non-homogeneity. Report as percent SiO_2, Fe_2O_3, Al_2O_3, $CaCO_3$ and $MgCO_3$.

TABLE 1 CONDITIONS

Condition Code	kV	mA	Secondary Target	Acquire ATM	Time(sec)	eV/ Channel
1	4.600	0.150	Direct	Vac	500.	10
2	25.000	2.350	AL	Vac	500.	10
3	23.000	0.970	GE	Vac	500.	10
4	15.000	0.850	TI	Vac	500	10

TABLE 2 DECONVOLUTIONS

Condition Code 1	Al, Si, P
Condition Code 2	Na, Mg
Condition Code 3	Ti, Mn, Fe
Condition Code 4	K, Ca

5.0 QUANTIFICATION CALCULATIONS:

Program quantifies data by using a least squares program. Similar samples with known chemical makeups are used as standards in the quantification technique. As many standards as possible are used for best quantification. The results are reported as oxides

in weight percents.

~~5.1 Calculations are shown in each part of the procedure in conjunction with the relevant analytical component.~~

~~5.2 In the analysis of slags, calcium and magnesium should be presented as calculated in terms of both carbonates and oxides.~~

6. REPORT:

6.1. % Insolubles: for all fine aggregate materials

6.2. % Silica: upon request only

6.3. % Combined Oxides for all except "silica" sand. ($Al_2O_3 + TiO_2 + MnO + Fe_2O_3$)

6.4. % $CaCO_3$: for all except "silica" sand

6.5. % $MgCO_3$: for all except "silica" sand

6.6. % CaO: for slags only

6.7. % MgO: for slags only

*NOTE: Program 9 includes the following: One oxidation for 2 minutes, temperature 1100°C, power of generator 77, agitation angle 25, and agitation speed 10. One fusion for 6 minutes, temperature 1100°C, power of generator 77, agitation angle 50, and agitation speed 15. Then there is a pause before casting for 10 seconds at a temperature of 1100°C. Casting lasts 2 minutes, temperature 1100°C, casting angle 123, casting speed 10 and time for solidification is 30 seconds. Lastly, there is natural cooling for 1 minute and forced air cooling for 3 minutes at a flow rate of 40. The setting of the dish height dial is 40/12 and this depends on the size of the platinum dish used.

APPROVED _____
Director
DIVISION OF MATERIALS

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